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(71) Applicant: HALLIBURTON COMPANY
P.O. Drawer 1431
Duncan Oklahoma 73536(US)

(72) Inventor: Brothers, Lance Everett
28 Quail Drive Route No. 1
Ninnekah Oklahoma 73036(US)
Inventor: Burkhalter, John Fred
1803 Parkview
Duncan Oklahoma 73533(US)

(74) Representative: Wain, Christopher Paul et al
A.A. THORNTON & CO. Northumberland
House 303-306 High Holborn
London WC1V 7LE(GB)

(54) Well cementing compositons.

(57) Low fluid loss salt-saturated cement slurries for oil and gas well cementing operations, comprise hydraulic cement; salt-saturated water present in an amount sufficient to form a pumpable slurry; and a fluid loss-reducing complex comprised of the reaction product of polyethyleneimine having a molecular weight above about 50,000 and one or more sulfonated organic compounds selected from lignosulfonic acid salts having Na, Ca or NH_4 as the associated cation and naphthalene sulfonic acid condensed with formaldehyde, having a molecular weight above about 5,000.

EP 0 261 883 A2

BNSDOCID: <EP_________0261883A2_I_>

WELL CEMENTING COMPOSITIONS

The present invention relates to well cementing compositions, more particularly to low fluid loss salt-saturated cement slurries and their use in oil and gas well cementing operations.

In oil and gas well primary cementing, a hydraulic cement slurry is pumped down a well bore penetrating a subterranean formation through a steel conduit disposed in the well bore, and back up through the annulus between the conduit and the well bore. Upon setting, the cement bonds and supports the conduit within the well bore and prevents fluid movement between subterranean formations penetrated by the well bore. To be useful as an oil field cementing slurry, the cement slurry, among other things, must be capable of allowing adequate placement time before setting, have low viscosity while being pumped, resist fluid loss into subterranean formations, have low free water separation and have rapid short-term strength development.

In a number of primary cementing applications, the use of aqueous salt saturated cement slurries is advantageous. The salt, generally sodium chloride, functions as a dispersant in the slurry, and causes the slurry to expand upon setting whereby the attainment of a good bond between the well bore and casing upon setting of the slurry is enhanced. In addition, aqueous salt-saturated cement slurries help prevent the swelling of clays and the sloughing of salt-contaning shale and other formations which in turn prevent problems such as bridging and lost circulation.

In remote or offshore locations where the availability of bulk blending equipment is limited, liquid fluid loss reducing additives for forming low fluid loss cement slurries are advantageous. Such liquid additives can be added directly to the water to form the slurry without the need for special mixing equipment.

The present invention provides low fluid loss, low viscosity aqueous salt-saturated cement slurries comprised of hydraulic cement, salt-saturated water present in an amount sufficient to form a pumpable slurry, and a fluid loss reducing complex comprised of the reaction product of polyethyleneimine having a molecular weight above about 50,000 and at least one sulfonated organic compound. The sulfonated organic compound is selected from lignosulfonic acid salts having Na, Ca, or NH_4 as the associated cation, and naphthalene sulfonic acid condensed with formaldehyde having a molecular weight above about 5,000. Mixtures of such compounds may be used.

The cement slurries can be prepared by directly combining the individual chemicals forming the reaction product i.e. the polyethyleneimine and sulfonated organic compound(s) can be combined directly with the mixing water utilized prior to combining hydraulic cement and salt therewith; or a liquid fluid loss reducing additive of the present invention described hereinbelow can be combined with the mixing water. The individual chemicals cannot be combined with the mixing water after the salt has been combined therewith because the fluid loss reducing reaction product will not adequately form in the presence of the salt.

The liquid fluid loss reducing additives of this invention are comprised of water, a base present in the water in an amount sufficient to raise the pH thereof to a level in the range of from about 13 to about 14, polyethyleneimine having a molecular weight above about 50,000 and at least one sulfonated organic compound selected from the group consisting of lignosulfonic acid salts having Na, Ca, or NH_4 as the associated cation and naphthalene sulfonic acid condensed with formaldehyde having a molecular weight above about 5,000.

Methods of using the low fluid loss aqueous salt saturated cement slurries of the invention for cementing oil and gas wells are also provided. The methods comprise introducing a low fluid loss aqueous salt saturated cement slurry into the annulus between a conduit disposed in a well bore penetrating a subterranean formation and the well bore, and allowing the slurry to set therein.

The slurries have reasonable thickening times, low free water values, good rheological properties, exhibit rapid short-term strength development and have low fluid loss.

The low fluid loss aqueous salt saturated cement slurries of the present invention exhibit low water loss to permeable formations contacted by the slurries during and after placement in a zone to be cemented. Once placed, the slurries set into hard masses having required strengths and other characteristics.

While various hydraulic cements can be utilized in forming the slurries, Portland cements of the various types identified as API Classes A through H and J cements are commonly utilized. These cements are identified and defined in API Specification for Materials and Testing for Well Cements, API Spec. 10, 3rd Edition, July 1, 1986, of the American Petroleum Institute to which reference should be made for further details.

In the low fluid loss aqueous salt saturated cement slurries of this invention, the hydraulic cement is preferably an API Class A through H or J Portland cement, and the salt is generally sodium chloride.

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The mixing water for the slurries can be fresh water, brine or sea water, and the mixing water is salt saturated by the addition of salt thereto, either before or during mixing with the hydraulic cement. When sea water is utilized as the mixing water for a slurry, sodium hydroxide is combined therewith in an amount sufficient to precipitate magnesium ion present in the sea water as magnesium hydroxide prior to combining the other components of the slurry with the water.

The liquid fluid loss reducing additive of this invention which can be utilized to form a low water loss saturated salt slurry of the invention is comprised of the reaction product of one or more polyethyleneimines having a molecular weight above about 50,000, preferably 80,000, and one or more sulfonated organic compounds selected from the group consisting of lignosulfonic acid salts having Na, Ca, or NH_4 as the associated cation, and naphthalene sulfonic acid condensed with formaldehyde having a molecular weight above about 5,000.

As mentioned above, the polyethyleneimine and sulfonated organic compound can be added directly to the mixing water utilized for forming the cement slurry wherein they react to form the fluid loss reducing reaction product, but the water cannot be saturated with salt when the addition is made. That is, the addition of the individual chemicals which react to form the fluid loss reducing complex must be added to the water prior to saturating the water with salt, and most preferably, prior to combining the salt, hydraulic cement and any other components utilized in the slurry with the water.

The sulfonated organic compounds suitable for use in accordance with this invention are lignosulfonic acid salts, e.g sodium, calcium or ammonium lignosulfonates, and naphthalene sulfonic acid condensed with formaldehyde having a molecular weight above about 5000, preferably 8000. While, for reasons which are not presently understood, some experimentally prepared lignosulfonates were not operable, commercially available sodium, calcium or ammonium lignosulfonates and naphthalene sulfonic acid condensed with formaldehyde, either by themselves or in admixture, react with polyethyleneimine to form a polymer complex which functions to reduce fluid loss from aqueous salt saturated cement slurries.

The fluid loss reducing complex comprised of the reaction product of polyethyleneimine and the sulfonated organic compound or compounds used is preferably present in the cement slurry in an amount in the range of from about 0.25% to about 2% by weight of dry cement utilized, most prefer ably in an amount of about 1% by weight of dry cement utilized.

The relative quantities of the polyethyleneimine and sulfonated organic compound forming the reaction product can vary. Preferably, the polyethyleneimine is added in an amount in the range of from about 0.5% to about 1.5% by weight of the dry cement utilized, most preferably about 0.7% by weight, and the sulfonated organic compound or compounds are added in an amount in the range of from about 0.2% to about 0.5% by weight of dry cement utilized, most preferably about 0.3% by weight.

A particularly preferred low fluid loss aqueous salt saturated cement slurry of the present invention is comprised of hydraulic cement, sodium chloride saturated water present in an amount sufficient to form a pumpable slurry, and a fluid loss reducing complex comprised of the reaction product of polyethyleneimine having a molecurlar weight of about 80,000 and sulfonated organic compounds comprised of a mixture of sodium lignosulfonate having Na, Ca, or NH_4 as the associated cation and naphthalene sulfonic acid condensed with formaldehyde having a molecular weight of about 8,000. The fluid loss reducing complex formed is preferably present in the salt saturated cement slurry in an amount in the range of from about 0.25% to about 2% by weight of dry cement utilized, most preferably about 1% by weight. The complex is preferably the reaction product of polyethyleneimine added in an amount in the range of from about 0.5% to about 1.5% by weight of dry cement, most preferably about 0.7% by weight, sodium lignosulfonate added in an amount in the range of from about 0.1% to about 0.3% by weight of dry cement, most preferably about 0.15% by weight, and naphthalene sulfonic acid condensed with formaldehyde added in an amount in the range of from about 0.1% to about 0.3% by weight of dry cement, most preferably about 0.15% by weight.

The liquid fluid loss reducing additives which can be utilized to prepare the low fluid loss aqueous salt saturated cement slurries are preferably combined with the slurry mixing water prior to adding other components thereto. The liquid additives are comprised of water, a base present in the water in an amount sufficient to raise the pH thereof to a level in the range of from about 13 to about 14, and the reaction product formed from polyethyleneimine having a molecular weight above about 50,000 and a sulfonated organic polymer selected from the group consisting of sodium, calcium or ammonium lignosulfonates, naphthalene sulfonic acid condensed with formaldehyde having a molecular weight above about 5,000, and mixtures of such compounds.

BNSDOCID: <EP_____0261883A2_I_>

The water utilized for forming the additive must be fresh water. The base used to adjust the pH can be any suitable strongly basic compound such as sodium hydroxide, potassium hydroxide or ammonium hydroxide. The addition of the base and the corresponding increase in the pH of the water allow the additives to have relatively long shelf lives without appreciable phase separation.

Polyethyleneimine is preferably added to a liquid additive of this invention in an amount in the range of from about 7% to about 15% by weight of the additive, most preferably about 12% by weight, with the sulfonated organic compound being added in an amount in the range of from about 2% to about 8% by weight of the additive, most preferably about 5% by weight. The resulting fluid loss reaction product formed from the polyethyleneimine and sulfonated organic compound or compounds is present in the additive in an amount in the range of from about 9% to about 23% by weight of the additive.

The most preferred liquid fluid loss reducing additive of this invention is comprised of fresh water, sodium hydroxide present in the water in an amount sufficient to raise the pH thereof to a level of about 14, polyethyleneimine added to the additive in an amount in the range of from about 7% to about 15% by weight of the additive, most preferably about 12% by weight, sodium lignosulfonate added in an amount in the range of from about 1% to about 5% by weight of the additive, most preferably about 2.5% by weight, and naphthalene sulfonic acid condensed with formaldehyde having a molecular weight of about 8,000 added in an amount in the range of from about 1% to about 5% by weight of the additive, most preferably about 2.5% by weight.

In preparing a low fluid loss aqueous salt saturated cement slurry of the present invention using the liquid fluid loss reducing additive, the additive is combined with the mixing water in an amount in the range of from about 2% by weight to about 9% by weight of dry cement to be used, most preferably about 5% by weight of dry cement.

The low fluid loss salt saturated cement slurries of the present invention can include other components such as silica flour to prevent cement strength deterioration in high temperature environments and sodium silicate to prevent the formation of free water in the cement slurry and improve thickening times. When silica flour is used it is preferably present in the slurry in an amount in the range of from about 20% to about 40% by weight of dry cement used. When sodium silicate is used, it is preferably present in the slurry in an amount in the range of from about 1% to about 3% by weight of dry cement used.

In using a low viscosity aqueous salt saturated slurry of the present invention for the primary cementing of an oil or gas well, the slurry is introduced into the annulus between the well bore and a conduit disposed therein. Generally, a steel casing and/or liner is disposed in the well which can extend from the surface to the formation or to a point between the surface and the formation. In order to bond and support the casing and/or liner in the well bore and prevent communication between formations or to the surface by way of the annulus between the outside of the casing and the well bore, a cement slurry is pumped downwardly within the casing or liner to the bottom end thereof and then upwardly in the annulus. After placement in the annulus, the cement slurry sets into a hard mass whereby the casing or liner is sealingly bonded to the walls of the well bore.

In accordance with the method of the present invention, a conduit in a well bore penetrating a subterranean formation is cemented by introducing a low fluid loss, low viscosity aqueous salt saturated cement slurry of the present invention into the annulus between the conduit and the well bore and allowing the slurry to set therein.

In order to further illustrate the present invention and to facilitate a clear understanding of the slurries, additives and methods thereof, the following examples are given.

Example 1

Various aqueous salt saturated cement slurries are prepared comprised of salt saturated fresh water, cement, silica flour and a fluid loss reducing component comprised of polyethyleneimine having a molecular weight of about 80,000 and various sulfonated organic compounds. The slurries are tested for free water, fluid loss and thickening time in accordance with API standard procedures. The results of these tests are given in Table I below.

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TABLE I

Properties of 16.1 lb/gal (1.93 g/cm³) Cement Slurries Comprised of Class H Cement, Sodium Chloride Saturated Fresh Water, 35% by Weight (of dry cement) Silica Flour and Various Fluid Loss Reducing Complexes

Sulfonated Organic Compound Used, % by Weight of Dry Cement				Polyethyleneimine, Gallon per Sack (m^3 per kg) of Dry Cement Utilized [10]		180°F (82°C) Free Water (ml)	180°F/1000psi (82°C/6.89MPa) Fluid Loss (cc/30 min)	Thickening Time for 192°F (89°C) Liner Schedule (hours:minutes)
A[1]	B[2]	C[3]	D[4]	A[5]	B[6]			
1.75[7]	-	-	-	0.7 (.06)	-	-	B.O.[8]	--
1.75	-	-	-	0.7 (.06)	-	-	52	16:30+
-	-	1.0	-	0.6 (.05)	-	-	B.O.	--
-	-	1.8	-	0.7 (.06)	-	-	B.O.	--
-	1.4	-	-	0.7 (.06)	-	-	325[11]	--
-	1.7	-	-	0.7 (.06)	-	-	92	1:16
-	2.0	-	-	0.7 (.06)	-	-	147[11]	--
-	1.7	-	-	0.8 (.07)	-	-	126[11]	--
-	1.7	-	-	0.5 (.05)	-	-	258[11]	--
0.8	0.9	-	-	0.7 (.06)	-	1	12	6:00+
0.6	0.7	-	-	0.5 (.05)	-	0	18	21:30+
0.4	0.44	-	-	0.7 (.06)	-	0	40	13:26
0.4	0.44	-	-	0.35 (.032)	-	-	329[11]	--
0.2	0.6	-	-	0.5 (.05)	-	-	184[11]	--
-	0.7	0.6	-	0.5 (.05)	-	-	B.O.	--
-	1.7	-	-	-- --	0.7(.06)	-	B.O.	--
0.4	0.44	-	-	-- --	0.5(.05)	high[9]	18	6:45+
-	0.44	-	0.4	-- --	0.5(.05)	high	--	7:24
-	0.44	-	0.4	0.5 (.05)	-	high	--	--
-	0.8	-	0.8	0.5 (.05)	-	high	--	--
0.2	1.7	-	-					

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NOTES TO TABLE I

1 Sulfonated organic compound A is calcium lignosulfonate.

2 Sulfonated organic compound B is naphthalene sulfonic acid condensed with formaldehyde having a molecular weight of about 8,000.

3 Sulfonated organic compound C is naphthalene sulfonic acid condensed with formaldehyde having a molecular weight of about 2500.

4 Sulfonated organic compound D is sodium lignosulfonate.

5 Polyethyleneimine A is a blend of polyethyleneimine having a molecurlar weight of about 80,000 and polyvinylpyrrolidone.

6 Polyethyleneimine B is substantially pure polyethyleneimine having a molecular weight of about 80,000.

7 Dry blended in cement. All other tests were conducted by predissolving the sulfonated material in the mix water, adding the polyethyleneimine and, finally, the dry blended cement, salt and silica flour.

8 Blew out immediately.

9 No definite boundary between fluid which did and did not contain cement particles. However, these slurries were characterized by unacceptable density segregation within the 250 ml graduated cylinder.

10 One (1) sack equals 94 pounds (42.3 kg) of cement.

11 Computed value.

From Table 1 it can be seen that lignosulfonic acid salts and naphthalene sulfonic acid condensed with formaldehyde having a molecular weight of about 8,000 achieve the best results. In addition, it can be seen that naphthalene sulfonic acid condensed with formaldehyde having a molecular weight of about 2500 does not function to produce a fluid loss reducing complex.

Example 2

The procedure of Example 1 is repeated utilizing different combinations of sulfonated organic compounds. Standard API viscosity and compressive strength tests are also carried out on the slurries. The results of these tests are given in Table II below.

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TABLE II

Properties of 16.0 lb/gal (1.92 g/cm³) Cement Slurries Comprised of Class H Cement, Sodium Chloride Saturated Fresh Water, 35% by Weight (dry cement) Silica Flour and Various Fluid Loss Reducing Complexes[3]

Test No.	Sulfonated Organic Compound Used, % by Weight of Dry Cement A[1]	Sulfonated Organic Compound Used, % by Weight of Dry Cement B[2]	Polyethyleneimine, gal. per Sack (m^3 per kg) of Dry Cement Utilized[4]	180°F (82°C) Free Water (ml)	180°F/1000 psi (82°C/6.89MPa) Fluid Loss (cc/30 min)	Thickening Time for 192°F (89°C) Liner Schedule (hrs:min)	Readings Taken at Various RPM's on a FANN Model 35A Viscometer at 180°F (82°C) 600 RPM	300 RPM	200 RPM	100 RPM	24 Hour Compressive Strength at 250°F (121°C) (psi)	(MPa)
1	0	0.8	0.5 (.05)	0.5	46(60)[5]	15:33	-	-	-	-	-	-
2	1.7	0	0.7 (.06)	-	92	1:16	-	-	-	-	-	-
3	0.4	0.4	0.5 (.05)	0.3	26	3:27	77	36	23	13	2690	18.5
4	0.5	0.5	0.5 (.05)	0(1.5)[5]	40	5:54	73	36	24	13	2860	19.7

1 Sulfonated organic compound A is naphthalene sulfonic acid condensed with formaldehyde having a molecular weight of about 8,000.
2 Sulfonated organic compound B is sodium lignosulfonate.
3 All tests were conducted by predissolving the sulfonated material in the mix water, adding the polyethyleneimine and, finally, the dry blended cement, salt and silica flour.
4 One (1) sack equals 94 pounds (42.3 kg) of cement.
5 Repeat test.

From Table II it can be seen that polyethyleneimine and a mixture of a lignosulfonic acid salt and naphthalene sulfonic acid condensed with formaldehyde having a molecular weight of about 8,000 produce cement slurries having excellent fluid loss and other properties.

BNSDOCID: <EP_____0261883A2_I_>

Example 3

The effect of mixing order on viscosity and fluid loss is determined for various cement slurries of the present invention. The mix water is sea water and various components are added to the sea water in various orders followed by cement and silica flour. The components added to the slurries and the amounts thereof are as follows:

Component	Amount Utilized	Identifying Designation Used in Table III
50% by wt. aqueous solution of NaOH	0.4 gal/barrel water (i.e. 0.4 volumes per 42 volumes water)	A
40% by wt. aqueous solution of a sodium lignosulfonate	0.12 gal/sack (0.01 m^3/kg) of cement	B
33% by wt. aqueous solution of naphthalene sulfonic acid condensed with formaldehyde having a MW of about 8,000	0.15 gal/sack (.014 m^3/kg) of cement	C
polyethyleneimine	0.4 gal/sack (.036 m^3/kg) of cement	D
NaCl	31% by weight of water	E

The results of these tests are given in Table III below.

BNSDOCID: <EP_______0261883A2_I_>

TABLE III

Effect of Mixing Order on Properties of 16.2 lb/gal (1.94 g/cm^3) Salt Saturated Sea Water Cement Slurries Comprised of Class G Cement, 35% by weight (of dry cement) Silica Flour and Various Fluid Loss Reducing Complexes

Order of Mix					165°F (74°C) Atmospheric Consistometer (Bc)		165°F (74°C) Fluid Loss (cc/30 min)
1st	2nd	3rd	4th	5th	Initial	20 Min	
A	B	C[1]	D	E	5	9	128[4]
A	C	B	D	E	5	8	158[4]
A	D	B	C	E	6	8	148[4]
E	A	B	C	D	15	17	594[4]
B	C	D	A	E	25	30	B.O.[2]
B	C	D	E	A	18	- 60[3]	--

[1] Prepared as a 33% solution.
[2] Blew out immediately.
[3] Attained 60 Bc after 2 minutes, test terminated.
[4] Computed value.

From Table III it can be seen that treating the water with a base prior to adding the components which form the fluid loss reducing complex and the salt reduces the viscosity of the slurry. Also, the components forming the fluid loss reducing complex must be added to the water prior to adding the salt.

Example 4

A liquid fluid loss reducing additive of the present invention is prepared by first combining sodium hydroxide with a quantity of fresh water to raise the pH to about 14. The additive is formed by combining polyethyleneimine in an amount of about 12% by weight of the additive, naphthalene sulfonic acid condensed with formaldehyde having a molecular weight of about 8,000 in an amount of about 2.5% by weight of the additive and a sodium lignosulfonate in an amount of about 2.5% by weight of the additive with the caustic water. The resulting additive contains the fluid loss reducing reaction product in an amount of about 17% by weight of the additive.

Portions of the additive described above are combined with salt saturated sea water to which a small amount of 50% sodium hydroxide is added. The water is then utilized to form a cement slurry by combining cement and silica flour therewith. The resulting slurries are tested for fluid loss, thickening time, viscosity, free water and compressive strength in accordance with standard API procedures. The results of these tests are set forth in Table IV below.

BNSDOCID: <EP_____0261883A2_I_>

TABLE IV

Properties of 16.1 lb/gal (1.93 g/cm³) Salt Saturated Sea Water Cement Slurries Comprised of Class G Cement, 35% by Weight (dry cement) Silica Flour and Fluid Loss Reducing Additive

Fluid Loss Additive (gal/sk/gal/10 bbl)[1]	Mix Water (gal/sk) (m^3/kg)	50% NaOH (gal/bbl) (1 vol per 42 vols)	Fluid Loss 126°F/1000 psi (52°C/6.89 MPa) (cc/30 min)	Thickening Time-126°F (52°C)(hrs:min)	Atmospheric Consistometer (Bc) Init	20 min	80°F (27°C) Free Water (%)	24Hr/126°F (52°C) Compressive Strength (psi)	(MPa)
0.53/30.6	6.7 (.60)	0.25	140[2]	7:37	3[3]	3[3]	0.5	1410	(9.7)
0.53/30.6	6.7 (.60)	0	992[6]	-	11[3]	6[3]	-	-	-
0.62/35.9	6.6 (.59)	0.25	145	4:02	3[4]	3[4]	-	2140	(14.7)
0.79/44.9	6.4 (.58)	0.25	130	4:05	3[5]	3[5]	-	-	-

1 Gal/10 bbl total mixing solution, e.g., 42 gal fluid loss additive per 378 gal mix water is expressed as 42 gal/10 bbl.
2 Average of 3 tests, 146, 146, 128 cc/30 minutes.
3 At a simulated BHCT of 126°F (52°C) (7000 ft.(2130 m) casing).
4 At a simulated BHCT of 150°F (66°C) (8670 ft.(2640 m) casing).
5 At a simulated BHCT of 167°F (75°C) (10,200 ft.(3110 m) casing).
6 Computed value.

BNSDOCID: <EP________0261883A2_I_>

From Table IV it can be seen that the fluid loss reducing additive of the present invention is effective in forming low fluid loss aqueous salt saturated cement slurries.

Example 5

The fluid loss additive described in Example 4 is used to form cement slurries having various quantities of silica flour, calcium lignosulfonate and sodium silicate included therein. The slurries are tested for free water, fluid loss, thickening time and compressive strength in accordance with standard API procedures. The results of these tests are given in Table V below.

BNSDOCID: <EP_____0261883A2_I_>

TABLE V

Properties of 16.5 lb/gal (1.98 g/cm³) Salt Saturated Sea Water Cement Slurries Comprised of Class G Cement

Mix Water[2] (gal/sk) (m³/kg)	Silica Flour (% by wt of cmt)	40% aqueous Solution of calcium Ligno-Sulfonate (gal/10 bbl) vols. per 420 vols	Sodium Silicate (gal/10 bbl) vols. per 420 vols	Liquid Fluid Loss Additive (gal/10 bbl) vols. per 420 vols	Atmospheric[1] Consistometer (Bc) Initial	Atmospheric[1] Consistometer (Bc) 20 Min	80°F (27°C) Free Water (%)	BHCT[3] Test Temp °F(°C)	Fluid Loss 325 Mesh(4) Screen 1000 psi (6.89MPa) (cc/30 minutes)	Thickening Time (Hours: Minutes)	Compressive Strength 24 Hours psi (MPa)
4.74 (.43)	0	0	3	42	5	5	0.4	126(52)	96	5:00	2980 (20.5)
5.7 (.51)	35	2	1.5	45	5	5	0.1	150(66)	135	5:45	2570 (17.7)
5.7 (.51)	35	2	1.5	45	4	7	0.1	167(75)	145	4:57	2440 (16.8)

1 Consistometer was preheated to BHCT.
2 3 gal/10 bbl (3 vols. per 420 vols.) of 50% by wt. NaOH added to sea water.
3 Fluid Loss, thickening time, and compressive strengths were determined at this temperature.
4 Sieve aperture 0.044 mm.

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The preceding examples can be repeated with similar success by substituting the generically or specifically described reactants of this invention for those used in the examples. From the foregoing description, one skilled in the art can easily ascertain the essential characteristics of this invention, and without departing from the spirit and scope thereof, can make various changes and modifications to adapt the invention to various usages and conditions.

Claims

1. A low fluid loss aqueous salt saturated cement slurry comprising hydraulic cement; salt-saturated water present in an amount sufficient to form a pumpable slurry; and a fluid loss-reducing complex comprised of the reaction product of polyethyleneimine having a molecular weight above about 50,000 and one or more sulfonated organic compounds selected from lignosulfonic acid salts having Na, Ca or NH_4 as the associated cation and naphthalene sulfonic acid condensed with formaldehyde, having a molecular weight above about 5,000.

2. A slurry according to claim 1, wherein the amount of said fluid loss-reducing complex in said slurry is from about 0.25% to about 2.0% by weight of dry cement.

3. A slurry according to claim 1 or 2, wherein said complex is comprised of the reaction product of said polyethyleneimine in an amount of from about 0.5% to about 1.5% by weight of dry cement and said sulfonated organic compound(s) in an amount of from about 0.2% to about 0.5% by weight of dry cement.

4. A slurry according to claim 1 or 2, wherein a mixture of sodium lignosulfonate and naphthalene sulfonic acid condensed with formaldehyde having a molecular weight of about 8,000, is used as the sulfonated organic compounds.

5. A slurry according to claim 4, wherein said complex is comprised of the reaction product of (1) said polyethyleneimine in an amount of from about 0.5% to about 1.5% by weight of dry cement, (2) said sodium lignosulfonate in an amount of from about 0.1% to about 0.3% by weight of dry cement, and (3) said naphthalene sulfonic acid condensed with formaldehyde in an amount of from about 0.1% to about 0.3% by weight of dry cement.

6. A slurry according to any of claims 1 to 5, wherein said salt-saturated water is sea water saturated with sodium chloride, and wherein said slurry also contains sodium hydroxide in an amount sufficient to precipitate any magnesium ion present in said sea water.

7. A slurry according to any of claims 1 to 6, which further includes silica flour in an amount of about 20% to about 40% by weight of dry cement.

8. A slurry according to any of claims 1 to 6, which further contains sodium silicate in an amount of from about 1.0% to about 3.0% by weight of dry cement.

9. A method of cementing a conduit in a well bore penetrating a subterranean formation, comprising introducing a slurry as claimed in any of claims 1 to 8, into the annulus between said conduit and said well bore, and allowing said slurry to set.

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(71) Applicant: HALLIBURTON COMPANY
P.O. Drawer 1431
Duncan Oklahoma 73536(US)

(72) Inventor: Brothers, Lance Everett
28 Quail Drive Route No. 1
Ninnekah Oklahoma 73036(US)
Inventor: Burkhalter, John Fred
1803 Parkview
Duncan Oklahoma 73533(US)

(74) Representative: Wain, Christopher Paul et al
A.A. THORNTON & CO. Northumberland House 303-306 High Holborn
London WC1V 7LE(GB)

(54) Well cementing compositons.

(57) Low fluid loss salt-saturated cement slurries for oil and gas well cementing operations, comprise hydraulic cement; salt-saturated water present in an amount sufficient to form a pumpable slurry; and a fluid loss-reducing complex comprised of the reaction product of polyethyleneimine having a molecular weight above about 50,000 and one or more sulfonated organic compounds selected from lignosulfonic acid salts having Na, Ca or NH_4 as the associated cation and naphthalene sulfonic acid condensed with formaldehyde, having a molecular weight above about 5,000.

EP 0 261 883 A3

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EUROPEAN SEARCH REPORT

Application Number

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X Y	US-A-4 482 383 (L.F. McKENZIE) * Claims 1,2; column 2, line 35 - column 4, line 9 * ---	1-3,9 4-6	E 21 B 33/13 C 04 B 28/04 C 04 B 24/18
X Y	US-A-4 482 381 (R.D. SPITZ) * Claims 1-10,13-22; column 4, lines 1-62 * ---	1-3,7-9 4-6	
Y	US-A-3 878 895 (D.R. WIELAND) * Claims 1-7,9-11 * ---	6	
Y	US-A-4 413 681 (L.F. McKENZIE) * Claims 1-4; column 2, line 40 - column 4, line 58 * -----	1-5,7,9	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			E 21 B C 04 B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	03-02-1989	ROTSAERT L.D.C.

CATEGORY OF CITED DOCUMENTS

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